Chapter 4
Hydraulic Fracturing Fluids

EPA reviewed information on fracturing fluids to identify and characterize potential threats to USDWs from any hazardous constituents that those fluids may contain. This chapter documents the information EPA gathered regarding the different types of fluids, their chemical composition, and the volumes and types of fluids used in each step of the fracturing process. EPA also estimated the concentrations of some fluid constituents to aid in the evaluation of level of threat posed to USDWs from fracturing fluids.

4.1 Introduction

Hydraulic fracturing fluids are used to initiate and propagate fractures, as well as transport proppant into fractures in coalbed formations to increase permeability and enhance methane production. Proppants are sand grains or other granular substances that are injected into the formation to hold or "prop" open coal formation fractures that have been created by hydraulic fracturing. Proppants wedged within the fracture serve to increase the permeability of the formation, which promotes liberation of the methane gas from the coal, and thereby enhances coalbed methane gas production. The fracturing fluids injected into the formation during hydraulic fracturing are subsequently pumped back out of the well in the process of extracting the methane gas and associated ground water. Some fracturing fluid may remain in the formation due to "leakoff" or due to the fluids being stranded in the formation.

The types and use of fracturing fluids have evolved greatly over the past 60 years. Their composition varies significantly, from simple water and sand, to complex polymeric substances with a multitude of additives. Service companies have developed a number of different oil and water-based fluids and treatments to more efficiently induce and maintain permeable and productive fractures. Water-based fracturing fluids have become the predominant type of coalbed methane fracturing fluids. In some cases, nitrogen or carbon dioxide gas is combined with the fracturing fluids to form foam as the base fluid. Foams perform comparably to liquids, but require substantially lower volumes to transport an equivalent amount of proppant. A variety of other fluid additives (in addition to the proppants) may be included in the fracturing fluid mixture to perform essential tasks such as formation clean-up, foam stabilization, leakoff inhibition or surface tension reduction.

Based on the availability of the scientific literature, it is evident that hydraulic fracturing fluid performance became a prevalent research topic in the late 1980's and the 1990's. Most of the literature pertaining to these fracturing fluids relates to the fluids' operational efficiency rather than the potential ramifications of their use relative to environmental or human health concerns. There is very little documented research on the environmental impacts that result from the injection and migration of these fluids into subsurface formations, soils and underground sources of drinking water (USDWs). Some of the existing research does offer information regarding the basic chemical components present in most of these fluids. EPA analyzed this information to determine whether contamination of USDWs could result from hydraulic fracturing fluid injection. EPA also witnessed hydraulic fracturing events in Kansas, Colorado and the western Virginia. Information was collected at these site visits for the purposes of this report. Figures 4-1 through 4-11, included at the end of this chapter, are captioned photographs showing the use of fracturing fluids at a coalbed methane well. These photographs are included to help the reader visualize of the hydraulic fracturing fluid volumes and the equipment required to inject and extract these fluids.

4.2 Chemical Constituents in Fracturing Fluids

The main goal of coalbed hydraulic fracturing is to achieve a highly conductive fracture. Fracturing fluids are formulated to provide sufficient viscosity to transport and place proppant into a fracture, and should degrade or "break" into a low viscosity fluid to allow for rapid flow-back and clean up. Breaking of the high viscosity fluid can be facilitated using pre-mixed additives within the fracturing fluid or by injecting breaker fluids into the well after the fracturing process is complete. Specifically, the following four qualities are desirable (adapted from Powell et al., 1999):

- Fluid must be viscous enough to create a fracture of adequate width;
- Fluid must possess characteristics that maximize fluid travel distance to extend fracture length;
- Fluid must be able to transport large amounts of proppant into the fracture; and
- Fluid must require minimal gelling agent to allow for easier breaking and reduced cost.

EPA identified fluids and fluid additives commonly used to create fractures through literature searches, material safety data sheets (MSDSs) provided by service companies, and discussions with field engineers, service company chemists and state government employees. On any one fracturing job, different fluids may be used in combination or alone at different stages in the fracturing process. The main fluid categories are:

- linear gels;
- cross-linked gels;
- foamed gels;
- plain water & potassium chloride (KCl)-water;
- acids; and
- combination treatments (any combination of 2 or more of the aforementioned fluids).

Fracturing fluids require additives to function efficiently, to maintain stability and to allow for easy recovery of the fluid for clean up. These additives include biocides, fluid-loss agents, enzyme breakers, acid breakers, oxidizing breakers, friction reducers, and surfactants, such as emulsifiers and non-emulsifiers. Several products may exist within each of these categories.

Many of the fluids and fluid additives contain constituents of concern. Table 4-1 lists product types, the chemical composition, and potential human health effects associated with the product. The information in Table 4-1 is from material safety data sheets provided by service companies. It is important to note that information presented in MSDSs is for pure product. Each of the products listed in Table 4-1 is significantly diluted prior to injection.

In order to evaluate the potential threat to human health, EPA estimated point-of-injection concentrations of fracturing fluid chemicals at the point of injection and within 100 feet of an idealized fracture radius. Table 4-2 presents estimated concentrations and maximum contaminant levels (MCLs) or ground water standards published by Massachusetts, for comparison. EPA used Massachusetts ground water standards because Massachusetts has developed standards for most constituents of concern in diesel.

The following example illustrates how EPA estimated the concentration of benzene, a constituent found in diesel fuel, at the point of injection. EPA used this calculation to estimate the concentrations at point of injection for all the chemicals we identified in fracturing fluids.

Based on MSDS information, linear gel can consist of 60% by weight diesel. According to the International Programme on Chemical Safety's Environmental Health Criteria 171 (IPCS, a joint venture of the United Nations Environment Programme, the International Labour Organisation, and the World Health Organization), diesel contains 0.0060% by weight benzene (IPCS website, 2002). According to industry sources, one recipe for CBM fracturing fluid is 10 gallons of linear gel to 1,000 gallons of water (Hudson, BJ Services, personal communication, 2002). The concentration at the point of injection of benzene in fracturing fluid can be calculated using the density of the diesel/gel mixture (assumed to be similar to the density of diesel fuel = 0.87 g/mL), the overall density of the injectate, or gel/water mixture (1 g/mL), the percent by weight fractional content of benzene in diesel fuel (0.006%), the percent by weight fractional content of diesel fuel in the gel mix (60%), and the mix ratio at which the diesel fuel is being diluted prior to injection (10 gallons of gel mix per 1000 gallons of water). It can be assumed that the density of the gel/water mixture, or the injectate, will be very close to that of plain water (10^9 μg/L). As shown in the equation below, the concentration of benzene in the total mixture is 313 μg/L.

$$[benzene]_{point\_of\_injection} = \frac{\left(10gal_{gel}\right)\left(0.87\frac{g}{mL}\right)\left(\frac{0.006g_{benzene}}{100.00g_{diesel}}\right)\left(\frac{60.00g_{diesel}}{100.00g_{gel}}\right)}{\left(1000gal_{gel+water}\right)\left(1.0\frac{g}{mL}\right)} \times 10^9\frac{\mu g}{L} = 313\frac{\mu g}{L}$$

The volumes of chemicals used in fracturing fluids vary among companies and from job to job. EPA found that most recipes result in concentrations on the same order of magnitude. The estimated concentrations presented in Table 4-2 were calculated using the mid-range volumes identified through discussions with service companies. In some cases, no chemicals are added to the water-based fracturing fluid.

The charge of this phase of the study did not include a formal fate and transport analysis. However, to further inform our decision, EPA calculated the effects of dilution on the concentrations of chemicals used in fracturing fluids at the edge of the fracturing zone. We assumed a fracture length of 1,500 feet, and a height of 200 feet. We also assumed a leak-off rate of 40%. Assuming that 40% will not be recovered during flow back, the concentrations of constituents at the edge of the fracture zone are approximately 30 times lower than when introduced at the point of injection (Table 4-2). In many cases, constituent concentrations were reduced to at or below ground water standards.

The Wyoming State Bureau of Land Management Record of Decision published an Environmental Impact Statement for the South Baggs Area of Carbon County detailing potential environmental impacts from coalbed methane development (U.S. Department of the Interior, WY State BLM, 2000). Table 4-3 is a duplicated list of chemicals identified by the BLM as hazardous compounds that may be in fracturing fluids. EPA identified similar chemicals through its search with the exception of MTBE. We found no information in the literature, MSDSs, or through interviews with service companies indicating that MTBE is a constituent in fracturing fluids used to stimulate coalbed methane wells.

The evolution of fracturing fluids and each of the major fracturing fluids and fluid additives is described in greater detail in the following sections.

Table 4-1: Summary of MSDSs for Hydraulic Fracturing Fluid Additives

Product	Chemical Composition Information[1]	Hazards Information	Toxicological Information	Ecological Information
Linear gel delivery system	1) 30-60% by wt. Guar gum derivative 2) 60-100% by wt. Diesel	-Harmful if swallowed -Combustible	-Chronic effects/Carcinogenicity - contains diesel, a petroleum distillate (known carcinogen) -Can cause skin disorders -Can be fatal if ingested	- Slowly biodegradable
Water gelling agent	1) 60-100% by wt. Guar gum 2) 5-10% by wt. Water 3) 0.5-1.5% by wt. Fumaric acid	- None	- May be mildly irritating to eyes	- Biodegradable
Linear gel polymer	1) <2% by wt. Fumaric acid 2) <2% by wt. Adipic acid	- Flammable vapors	- Can cause eye, skin and respiratory tract irritation	- Not determined
Linear gel polymer slurry	1) 30-60% by wt. Diesel oil #2	- Causes irritation if swallowed - Flammable	- Carcinogenicity – Possible cancer hazard based on animal data; diesel is listed as a category 3 carcinogen in EC Annex I - May cause pain, redness, dermatitis	- Patially biodegradable
Crosslinker	1) 10-30% by wt. Boric Acid 2) 10-30% by wt. Ethylene Glycol 3) 10-30% by wt. Monoethanolamine	-Harmful if swallowed -Combustible	-Chronic effects/Carcinogenicity D5 may cause liver, heart, brain reproductive system and kidney damage, birth defects (embryo and fetus toxicity) -Causes eye, skin, respiratory irritation -Can cause skin disorders and eye ailments	- Not determined
Crosslinker	1) 10-30% by wt. Sodium tetraborate decahydrate	- may be mildly irritating to eyes and skin - may be mildly irritating if swallowed	- May be mildly irritating	- Partially biodegradable - Low toxicity to fish
Foaming agent	1) 10-30% by wt. Isopropanol 2) 10-30% by wt. Salt of alkyl amines 3) 1-5% by wt. Diethanolamine	- Harmful if swallowed - Highly flammable	- Chronic effects/Carcinogenicity – may cause liver and kidney effects - Causes eye, skin, respiratory irritation - Can cause skin disorders and eye ailments	- Not determined
Foaming agent	1) 10-30% by wt. Ethanol 2) 10-30% by wt. 2-Butoxyethanol 3) 25-55% by wt. Ester salt 4) 0.1-1% by wt. Polyglycol ether 5) 10-30% by wt. Water	- Harmful if swallowed or absorbed through skin	- May cause nausea, headache, narcosis - May be mildly irritating	- Harmful to aquatic organisms
Acid treatment - hydrochloric acid	1) 30-60% by wt. Hydrochloric acid	- May cause eye, skin and respiratory burns - Harmful if swallowed	- Chronic effects/Carcinogenicity – prolonged exposure can cause erosion of teeth - Causes severe burns - Causes skin disorders	- Not determined
Acid treatment - formic acid	1) 85% by wt. Formic acid	- May cause mouth, throat, stomach, skin and - May cause genetic changes	- May cause heritable genetic damage in humans - Causes severe burns - Causes tissue damage	- Not determined
Breaker Fluid	1) 60-100% by wt. Diammonium peroxidisulphate	-May cause respiratory tract, eye or skin irritation - Harmful if swallowed	- May cause redness, discomfort, pain, coughing, dermatitis	- Not determined
Microbicide	1) 60-100% by wt. 2-Bromo-2nitro1,3-propanedol	- May cause eye and skin irritation	- Chronic effects/Carcinogenicity – not determined - Can cause permanent eye damage, skin disorders, abdominal pain, nausea, and diarrhea if ingested	- Not determined
Biocide	1) 60-100% by wt. 2,2-Dibromo-3-nitrilopropionamide 2) 1-5% by wt. 2-Bromo-3-nitrilopropionamide	- Causes severe burns - Harmful if swallowed - May cause skin irritation - May cause allergic reaction upon repeated skin exposure	-Harmful if swallowed; large amounts may cause illness - Irritant; may cause pain or discomfort to mouth, throat, stomach; may cause pain, redenss, dermatitis	- Not determined
Acid corrosion inhibitor	1) 30-60% by wt. Methanol 2) 5-10% by wt. Propargyl alcohol	- May cause eye and skin irritation, headache, dizziness, blindness and central nervous system effects - May be fatal if swallowed - Flammable	- Chronic effects/Carcinogenicity – may cause eye, blood, lung, liver, kidney, heart, central nervous system and spleen damage - Causes severe eye, skin, respiratory irritation - Can cause skin disorders	- Not determined
Acid corrosion inhibitor	1) 30-60% by wt. Pyridinium, 1-(Phenylmethyl)-, Ethyl methyl derivitives, Chlorides 2) 15% by wt. Thiourea 3) 5-10% Propan-2-ol 4) 1-5% Poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy 5) 10-30% Water	- Cancer hazard (risk depends on duration and level of exposure) - Causes severe burns to respiratory tract, eyes, skin - Harmful if swallowed or absorbed through the skin	- Carcinogenicity – Thiourea is known to cause cances in animals, and possibly causes cancer in humans - Corrosive - short exposure can injure lungs, throat, and mucous membranes; can cause burns, pain, redness swelling and tissue damage	- Toxic to aquatic organisms - Patially biodegradeable

[1] MSDS chemical composition percentages may total more than 100%

Table 4-2. Estimated Concentrations at the Point of Injection of Constituents of Concern in Hydraulic Fracturing Fluids

Product	Chemical Composition of Existing Products	Concentrations of Interest (ug/L)	
	Chemical Compound	Injection Concentration	MCL or RBC or MCP
Linear gel delivery system	guar gum derivative		
	diesel		
	benzene	313.20	5.00
	toluene	522.00	1,000.00
	ethylbenzene	522.00	700.00
	xylene	522.00	10,000.00
	napthalene	14,094.00	20.00
	1-methylnapthalene	71,340.00	20 / 6,000
	2-methylnapthalene	34,974.00	121.67
	dimethylnapthalenes	270,570.00	na
	trimethylnapthalenes	160,080.00	na
	fluorenes	31,320.00	2,190.00
	phenanthrenes	7,830.00	300 / 50
	aromatics	574,200.00	200 / 30,000
Water gelling agent	guar gum		
	water	495,049.50	na
	fumaric acid	132,337.87	na
Linear gel polymer	fumaric acid	529,351.49	na
	adipic acid	366,257.43	na
Gelling agents (BLM Lists)	benzene		5.00
	ethylbenzene		700.00
	methyl tert-butyl ether		2.64
	napthalene		20.00
	polynuclear aromatic hydrocarbons (PAHs)		na
	polycyclic organic matter (POM)		na
	sodium hydroxide		na
	toluene		1,000.00
	xylene		10,000.00
Crosslinker	boric acid	170,998.00	na
	ethylene glycol	285,788.42	73,000.00
	monoethanolamine	na	na
Crosslinker	sodium tetraborate decahydrate	na	na
Crosslinkers (BLM Lists)	ammonium chloride		na
	potassium hydroxide		na
	zirconium nitrate		na
	zirconium sulfate		na
Foaming agent	isopropanol	234,945.16	na
	salt of alkyl amines	na	na
	diethanolamine	na	na
Foaming agent	ethanol	236,081.75	na
	2-butoxyethanol	269,641.08	na
	ester salt	na	na
	polyglycol ether	na	na
	water		na
Foamers (BLM Lists)	glycol ethers		na
Acid treatment - hydrochloric acid	hydrochloric acid	na	na
Acid treatment - formic acid	formic acid	na	73,000.00
Breaker Fluid	diammonium peroxidisulphate	na	na
Breaker Fluids (BLM Lists)	ammonium persulfate		na
	ammonium sulphate		na
	copper compounds		1,460.00
	ethylene glycol		na
	glycol ethers		na
Microbicide	2-bromo-2nitro1,3-propanediol	na	na
Biocide	2,2-dibromo-3-nitrilopropionamide	na	na
	2-bromo-3-nitrilopropionamide	na	na
Bactericides	polycyclic organic matter (POM)	na	na
	polynuclear aromatic hydrocarbons (PAHs)	na	na
Acid corrosion inhibitor	methanol	236,070,000.00	18,250.00
	propargyl alcohol	47,425,000.00	na
Acid corrosion inhibitor	pyridinium, 1-(phenylmethyl)-, ethyl methyl deriv	na	na
	thiourea	210,750,000.00	na
	propan-2-ol	39,275,000.00	na
	poly(oxy-1,2-ethanediyl)-nonylphenyl-hydroxy	na	na
	water		na

(green)	= 2 numbers given (1. Drinking water standard 2.Groundwater discharging to surface water standard)
(yellow)	= Exceeds regulatory standard
MCL	= Maximum Contaminant Level - The highest level of a contaminant that is allowed in drinking water.
RBC	= EPA's Risk Based Concentration Tables. www.epa.gov/reg3hwmd/risk/index.html, developed by Region 3 (serving: Delaware, District of Columbia, Maryland, Pennsylvania, Virginia, West Virginia)
MCP	= Massachusetts Contingency Plan - Risk-based ground water standards for drinking water protection - chosen because Massachusetts has developed standards for many constituents in diesel fuel

Table 4-3. Summary of Hydraulic Fracturing Fluids and Additives from BLM Lists

Product	Chemical Constituents (as identified by BLM)
Gelling agents	benzene ethylbenzene methyl tert-butyl ether napthalene polynuclear aromatic hydrocarbons (PAHs) polycyclic organic matter (POM) sodium hydroxide toluene xylene
Crosslinkers	ammonium chloride potassium hydroxide zirconium nitrate zirconium sulfate
Foamers	glycol ethers
Breaker Fluids	ammonium persulfate ammonium sulphate copper compounds ethylene glycol glycol ethers

4.3 History of Fracturing Fluids

John W. Ely published a comprehensive history of the evolution of hydraulic fracturing fluids in the oil and gas industry in a 1985 book entitled *The Handbook of Stimulation Engineering*. *The Handbook* was used as a source of information for this chapter, in addition to more recent scientific literature and personal communications with pertinent sources.

Formation fracturing using fluids has been employed by the oil and gas industry in the United States since the early 1940's (Ely, 1985). Early fracturing fluid technology involved injection of gelled napalm or fuel oil to increase oil and gas well production efficiency (Ely, 1985). These techniques were short-lived due to poor performance and the health hazards generally associated with the chemicals that were used early on. The next step in fracturing fluid evolution involved the use of gelled oils, fatty acids and caustic soaps (Ely, 1985). Because of the excessively high friction associated with these liquids, the industry moved toward the use of water without additives (Ely, 1985). However, water alone is not always adequate for fracturing certain formations since its low viscosity diminishes its ability to transport proppant. Higher viscosity fracturing fluids were needed to overcome this problem, so the industry developed thickened water starch and then guar-based fluids, also known as linear gels. Guar is a polymeric substance derived from the ground endosperm of the guar plant (Ely, 1985). Guar gum, on its own, is non-toxic and, in fact, is a food-grade product that is commonly used to increase the viscosity and elasticity of foods such as ice cream.

The success of guar-based fluids led to further advances in viscous liquid technology. Different guar derivatives were developed, the most popular being hydroxypropylguar (HPG) and carboxymethylhydroxypropylguar (CMHPG).

One major advance in fracturing fluid technology was the development of cross-linked gels. Cross-linking agents are added to linear gels in order to provide higher proppant transport performance relative to the linear gels (Ely, 1985; Halliburton Inc., Virginia Site Visit, 2001). Since the introduction of cross-linked fluids, improvements in these fluids have elevated the performance of fracturing treatments.

Another fracturing fluid that quickly gained popularity alongside the use of gelled fluids was foam fracturing. The most popular foam-fracturing fluids employ nitrogen or carbon dioxide as their base gas. The incorporation of inert gases with foaming agents and water diminished the requirement for large volumes of fracturing liquid. The gas bubbles in the foam fill voids that would otherwise be filled by fracturing fluid. Service companies reduce the liquid volume as much as 75 percent by using foams (Ely, 1985; Halliburton Inc., Virginia Site Visit, 2001). Foaming agents can be used in conjunction with gelled fluids to achieve an extremely effective fracturing fluid (Halliburton, Inc., Virginia Site Visit, 2001).

4.4 Types of Fluids

Each of these fluids is unique in nature, and each possesses its own positive and negative performance traits. Most of these fluids are water-based, however, they can also be oil, methanol, or water/methanol mixture based as well. Methanol is used in lieu of, or in conjunction with, water to minimize fracturing fluid leak-off and enhance fluid recovery (Thompson et al., 1991). “Methanol is a common winterizing agent in many additives and has been used in the base fluid of many fracturing treatments…”(GRI, 1996). Polymer-based fracturing fluids made with methanol usually improve fracturing results, but create a requirement for 50 to 100 times the amount of breaker (Ely, 1985). Methanol breakers are typically acids (Ely, 1985).

4.4.1 Gelled Fluids

Water gellants or thickeners are used to create linear and cross-linked fluids. Gellant selection is based upon formation characteristics such as pressure, temperature, permeability, porosity, zone thickness, etc. Both linear and cross-linked fluid fluids are described in the following sections.

Linear Gels

A substantial number of fracturing treatments are completed using thickened, water-based linear gels. The gelling agents used in these fracturing fluids are typically guar gum, HPG, CMHPG, carboxymethyl guar, hydroxyethylcellulose (HEC) or other cellulose derivatives. Guar, cellulose and their derivatives are polymeric substances used to increase the viscosity of the fracturing fluid. To formulate a gel fluid, guar powder or concentrate is dissolved into a carrier fluid so it can create the viscous fracturing liquid. Increased viscosity improves the ability of the fracturing fluid to transport proppant with less need for turbulence. Concentrations of guar gelling agents within fracturing fluids have decreased over the past several years. It was determined that reduced concentrations provide better and more complete breaks in a fracture (Powell et al., 1999).

Hydraulic fracturing gels are typically made up of a gel thickening agent and a carrier fluid. Examples of industrially produced gel thickeners include, hydroxypropylguar blends, guar gum blends, hydroxypropylcellulose, hydroxyethylcellulose, sodium carboxymethylcellulose and cellulose derivatives. In general, these products are biodegradable.

Gel thickeners are slurried into a carrier fluid such as water or diesel fuel. Diesel is frequently used in lieu of water to dissolve the guar powder because its carrying capacity per unit volume is much higher (Halliburton, Inc., 2002). "Diesel is a common solvent additive, especially in liquid gel concentrates, used by many service companies for continuous delivery of gelling agents in fracturing treatments" (GRI, 1996). Diesel does not enhance the efficiency of the fracturing fluid; it is merely a component of the delivery system (Halliburton, Inc., 2002). Using diesel instead of water minimizes the number of transport vehicles needed to carry the liquid gel to the site (Halliburton, Inc., 2002).

The percentage of diesel fuel in the slurried thickener can range between 30% up to near 100% based on the MSDSs summarized in Table 4-1. Diesel is a petroleum distillate, many of which contain known carcinogens. One such component of diesel is benzene, which, according to literature sources, can make up anywhere between 0.003 to 10.3 % by weight of diesel oil (Clark, R.C. and Brown, D. W. 1977; R. Morrison & Associates, Inc., 2001). Slurried diesel and gel is diluted with water prior to injection into the subsurface. The dilution concentration is approximately four to six gallons of concentrated liquid gel (guar slurried in diesel) per 1,000 gallons of make-up water to produce an adequate polymer slurry (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001, Written Correspondence).

Some gelling agents can contain several hazardous substances including benzene, ethylbenzene, methyl tert-butyl ether, napthalene, polynuclear aromatic hydrocarbons (PAHs), polycyclic organic matter (POM), sodium hydroxide, toluene, and xylene (U.S.

Department of the Interior, CO State BLM, 1998). Concentrations of these compounds within the fracturing fluids were not presented in the aforementioned reference. Information from material safety data sheets (MSDSs) for polymer-based gels is summarized in Table 4-1.

C*ross-linked Gels*

The first cross-linked gels were developed (Ely, 1985) in 1968. When cross-linking agents are added to linear gels, the result is a complex, high-viscosity fracturing fluid (Messina, Inc. website, 2001). Cross-linking reduces the need for fluid thickener, and extends the viscous life of the fluid indefinitely. The fracturing fluid remains viscous until a breaking agent is introduced to break the cross-linker, and eventually the polymer. Although they make the fluid more expensive, cross-linkers can considerably improve performance hydraulic fracturing performance, hence increasing coalbed methane well production rates.

Cross-linked gels are typically metal ion-cross-linked guar (Ely, 1985). Service companies have used metal ions, such as chromium, aluminum, titanium or other metal ions to achieve cross-linking (Ely, 1985). In 1973, low-residue (cleaner) forms of cross-linked gels were developed, such as cross-linked hydroxypropylguar (HPG) (Ely, 1985). Cross-linkers may contain hazardous constituents, including ammonium chloride, potassium hydroxide, zirconium nitrate, and zirconium sulfate (U.S. Department of the Interior, CO State BLM, 1998). Concentrations of these compounds within the fracturing fluids were not presented in the aforementioned reference.

Information from MSDSs for cross-linked gels is summarized in Table 4-1. The MSDSs were supplied by service companies and fluids manufacturers that are currently operating in the US. The products surveyed contained boric acid, sodium tetraborate decahydrate, ethylene glycol and monoethylamine. The constituents in the crosslinkers listed in Table 4-1 are proven to cause kidney, liver, heart, blood and brain damage through prolonged or repeated exposure. The final concentration is typically one to two gallons of cross-linker per 1,000 gallons of gel (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001, Written Correspondence).

Over a period of 30 minutes, 4,500 to 15,000 gallons of fracturing fluid will typically transport and place approximately 11,000 to 25,000 pounds of proppant into the fracture (Powell et al., 1999).

4.4.2 Foamed Gels

Foam fracturing is a technology that uses foam bubbles to transport and place proppant into fractures. Foams, which are gas-liquid emulsions, have nitrogen or carbon dioxide as the fluid’s gaseous component. The use of foams is regarded as one of the least environmentally damaging fracturing methods because these fluids utilize fracturing fluid with higher proppant concentrations to achieve highly effective fracturing. The high concentrations of proppant allow for an approximate 75% reduction in the overall amount of fluid that would otherwise be necessary using a conventional linear or cross-linked gel (Ely, 1985; Virginia Site Visit, 2001). Foams can also be cross-linked for enhanced performance results (Ely, 1985; Halliburton, 2001).

Foam fracturing treatments use nitrogen or carbon dioxide as the base gas for the foam. Foam emulsions experience high leak-off; therefore, typical protocol involves the addition of fluid loss agents, such as fine sands (Ely, 1985; Halliburton, 2001). Foaming agents suspend air, nitrogen, or carbon dioxide within the aqueous phase of a fracturing, acidizing, or gelled acid treatment. The gas/liquid ratio determines if a fluid will be true foam, or simply gas-energized (Ely, 1985). Carbon dioxide can be injected as a liquid while nitrogen must be injected as a gas to prevent freezing (Halliburton, Inc., 2002).

Information from MSDSs for foaming agents is summarized in Table 4-1. The foamers can contain diethanolamine, and alcohols, such as, isopropanol, ethanol, and 2-butoxyethanol (Table 4-1). They can also contain hazardous substances including glycol ethers (U.S. Department of the Interior, CO State BLM, 1998). Concentrations of these compounds within the fluids were not presented in the aforementioned reference.

Glycol ethers are hazardous substances. One of the foamer products surveyed can cause negative liver and kidney effects, although the actual component causing these effects is not specified on the MSDS. The final concentration is typically three gallons of foamer per 1,000 gallons of gel (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001, Written Correspondence).

4.4.3 Water & Potassium Chloride Water Treatments

Many service companies use ground water pumped directly from the formation or treated water to generate adequate fracture length. In some coalbed methane well stimulations, proppant use is not necessary to prop fractures open, so simple water or slightly thickened water can be a cost effective substitute for an expensive polymer or foam-based fracturing fluid with proppant (Ely, 1985). Hydraulic fracturing performance is not exceptional with plain water, but, in some cases, the production rates achieved are adequate. Plain water has a lower viscosity than gelled water, which reduces proppant transport capacity.

Similar to plain water, another fracturing fluid uses water with potassium chloride (KCl) containing small quantities of gelling agents, polymers and/or surfactants (Ely, 1985). Information from MSDSs for KCl or KCl substitutes is summarized in Table 4-1 Potassium chloride is relatively harmless if ingested at low concentrations.

4.4.4 Acids

Acids are used to dissolve minerals present in the formation that can restrict production. This leads to an increase in the permeability of the formation, and thus, an increase in production.

Typically, the acidic stimulation fluid is hydrochloric acid or a combination of hydrochloric and acetic or formic acid. In the field of coalbed methane production, acids are used in limestone formations that overlay or are interbedded within coals to dissolve the rock and create a conduit through which the gas can travel (Ely, 1985). For acid fracturing to be successful, thousands of gallons of the acid must be pumped far into the formation to etch the face of the fracture (Ely, 1985). Some of the same cellulose derivatives used in water and water/methanol fluids as gelling agents can be used in acid fluids to improve and increase treatment distance (Ely, 1985).

In coalbed methane well fracturing, acids can be used when limestone formations (adjacent to the coals) containing the coalbed methane need to be fractured. Acids are not used to stimulate coals directly (Wilson, VDMME, personal communication 2001). In coalbed methane production, acids can be used to clean up perforations of the cement surrounding the well casing prior to fracture fluid injection (Halliburton, Inc., Virginia Site Visit, 2001; Halliburton, Inc., Virginia Site Visit, 2002). The cement is perforated at the desired zone of injection to ease fracturing fluid flow into the formation (Halliburton, Inc., Virginia Site Visit, 2001; Halliburton, Inc., Virginia Site Visit, 2002). This may, or may not be common practice in the fracturing industry, however it is commonly used by Halliburton, Inc. in Virginia.

A variety of acids is used in traditional hydraulic fracturing treatments, including hydrochloric acid, hydrofluoric acid, acetic acid and formic acid. Information from MSDSs for acidic fluids used in hydraulic fracturing is summarized in Table 4-1. The acids used are typically formic acid and hydrochloric acid. Acids are corrosive, and can be extremely hazardous in concentrated form. Acids are substantially diluted prior to injection into the subsurface. The acids are mixed with water-based or water and gas-based fluids to dilute the product. The injected concentration is typically 1,000 times weaker than the concentrated versions presented in the product MSDSs (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001, Written Correspondence).

4.4.5 Combination Treatments

Service companies will often make use of a combination of two or more of the aforementioned treatments in combination to achieve their desired fracturing results. Depending on formation characteristics, experienced service company engineers will devise the most effective fracturing scheme using the fracturing fluid combination they deem most effective.

4.4.6 Fluid Additives

Several fluid additives have been developed to enhance the efficiency and increase the success of fracturing fluid treatments. The major categories of these additives are defined and briefly described in the following sections.

Breakers

Breaker fluids are used to degrade the fracturing fluid viscosity, which helps to enhance post fracturing fluid recovery, or flowback. As discussed in Chapter 3, natural or propagating fractures may open and allow fluids to flow through during high fracturing pressure, but may also subsequently trap the fluids as they close after fracturing pressure decreases (the “check-valve” effect) (Warpinski et al., 1988; Palmer et al., 1991a). Experiments performed by Stahl and Clark (1991) confirm that this phenomenon dominates fluid-loss behavior in coal beds. Contrary to conventional formations where “leak-off” and fluid invasion may penetrate only a few inches, stimulation fluids in coal penetrate from 50 to 100 feet away from the fracture and into the surrounding formation (Palmer et al., 1991; Puri et al., 1991). If a fracturing fluid is injected at very high pressure a great distance into a formation, and “leaks off” into secondary or existing fractures, it is possible that it will remain stranded if the flowback and production processes do not recover it.

EPA reviewed four papers that discuss flow back volumes. Palmer and others (1991a) conducted the only study conducted in coalbed environments. They reported that only 61 percent of fracturing fluids were recovered during a 19-day production sampling of a coalbed well in the Black Warrior basin, Alabama. Samuel et al. (1997) report that several studies relating to guar-based polymer gels document flow-back recovery rates of approximately 30-45%. The paper did not discuss the duration over which flow-back recovery rates were measured. Willberg et al. (1997) report that polymer recovery rates during flowback averaged 29-41% of the amount pumped into the fracture. The results from this study were derived from tests performed on 10 wells over periods of four or five days (Willberg et al., 1997). Willberg et al. (1998) report that polymer returns at conservative flow back rates averaged 25-37% of the amount pumped into the fracture, while returns at aggressive flow back rates averaged 37-55%. The results from this study were derived from tests performed on 15 wells over periods of two days at aggressive flow back rates and five days at conservative flow back rates.

Breakers can be mixed in with the fracturing fluid during pumping, or they can be introduced later as an independent fluid. There are a variety of breaker types including time-release and temperature dependent types. Most breakers are typically acids, oxidizers, or enzymes (Messina, Inc. website, 2001). Breakers may contain hazardous constituents, including ammonium persulfate, ammonium sulphate, copper compounds, ethylene glycol, and glycol ethers (U.S. Department of the Interior, CO State BLM, 1998). Concentrations of these compounds within the fracturing fluids were not presented in the aforementioned reference.

Biocides

One problem that arises when using organic polymers within fracturing fluids is the incidence of bacterial growth within the fluids. Due to the presence of organic constituents, the fracturing fluids provide a medium for bacterial growth. As the bacteria grow, they secrete enzymes that break down the gelling agent, which reduces the viscosity of the fracturing fluid. Reduced viscosity translates into poor proppant placement and poor fracturing performance. To alleviate this degradation in performance, biocides, bactericides, or microbicides are added to the mixing tanks with the polymeric gelling agents to kill any existing microorganisms, and to inhibit bacterial growth and deleterious enzyme production. These additives are used to kill microorganisms such as sulfate reducing bacteria, slime forming bacteria, and algae. Bactericides are typically hazardous by nature (Messina, Inc. website, 2001). They may contain hazardous constituents, including polycyclic organic matter (POM) and polynuclear aromatic hydrocarbons (PAHs) (U.S. Department of the Interior, CO State BLM, 1998). Concentrations of these compounds within the fracturing fluids were not presented in the aforementioned reference.

Information from MSDSs for a biocide and a microbicide is summarized in Table 4-1. These concentrated products are substantially diluted prior to injection into the subsurface. Typical concentration for dilution in the make-up water is one to two tenths of a gallon of microbicide in 1,000 gallons of water (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001, Written Correspondence).

Fluid-Loss Additives

Fluid loss additives restrict leak-off of the fracturing fluid into the exposed rock at the fracture face. By restricting leak-off, fracturing fluid effectiveness and integrity is maintained. Fluid loss additives of the past and present include bridging materials such as 100 mesh sand, 100 mesh soluble resin, and silica flour, or plastering materials such as starch blends, talc silica flour, and clay (Ely, 1985).

Friction Reducers

To optimize the fracturing process, aqueous fluids must be pumped at maximum rates and fluids must apply maximum hydrostatic pressure within the treatment process. Increasing flow velocities and pressures in this manner can lead to undesirable levels of friction within the infrastructure and the fracture itself. In order to minimize friction, friction reducers are added to aqueous-based fracturing fluids. These are typically latex polymers or copolymers of acrylamides. They are added to slick water treatments (water with solvent) at concentrations of 0.25-2.0 pounds per 1,000 gallons (Ely, 1985). Some examples of friction reducers include oil soluble anionic liquid, cationic polyacrilate liquid, and cationic friction reducer (Messina, Inc. website, 2001).

Acid Corrosion Inhibitors

Corrosion inhibitors are required in acid fluid mixtures because acids are corrosive to steel tubing, well casings, tools, and tanks. Acetone is a solvent that is commonly used as an additive in corrosion inhibitors (GRI, 1996). Information from MSDSs for acid inhibitors is summarized in the Table 4.1. These products can affect the liver, kidney, heart, central nervous system, and lungs. They are quite hazardous in their undiluted form. These products are diluted to a concentration of one gallon per 1,000 gallons of make-up water and acid mixture (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001, Written Correspondence). Acids and acid corrosion inhibitors are used in very small quantities in coalbed methane fracturing (500 to 2,000 gallons per treatment).

4.4.7 Proppants

The purpose of a proppant is to prop open a hydraulically created fracture. An ideal proppant should produce maximum conductivity in a fracture. Fracture conductivity is a function of proppant pack thickness (volume), roundness, purity and crush strength. In coalbed methane fracturing, the most predominantly used proppant is pure sand of varying mesh size.

4.5 Summary

Fracture engineers select fracturing fluids based on site-specific characteristics including formation geology, field production characteristics, and economics. Fracturing fluids vary widely with regard to the types of chemical additives used, the volumes of fluid required and the pump rates at which the fracturing fluids are injected. Based on the information EPA collected, water constitutes the solute in fracturing fluids used for coalbed methane stimulation. Other components of fracturing fluids used to stimulate coalbed methane wells may contain only benign ingredients, but in some cases, contain hazardous constituents.

Water with a simple sand proppant can be adequate to achieve a desired fracture. In some cases, water must be thickened to achieve higher proppant transport capabilities. Thickening can be achieved by using linear or cross-linked gelling agents. Cross-linkers are costly additives when compared to simple linear gels, but the fluid’s fracturing efficiency can be greatly improved using these additives. Foam fracturing fluids can be used to minimize injected fluid volumes considerably. The reduced water volume requirement translates into a space and cost savings at the treatment site because fewer water tanks are needed. Foam fracturing fluids also promote rapid flow-back and reduced disposal volumes of flow-back water.

The most notable contaminant in hydraulic fracturing fluids is diesel fuel used in the fracturing gels. Diesel contains known carcinogens. Diesel is a common solvent additive in liquid gel concentrates. It is used in lieu of water to dissolve the gelling powder because its carrying capacity per unit volume is much higher. Diesel does not enhance the efficiency of the fracturing fluid; it is merely a component of the delivery system. Using diesel instead of water minimizes the number of transport vehicles needed to carry the liquid gel to the site, and therefore reduces the cost of the fracturing event.

Table 4-1 presented in this chapter summarizes chemical constituents identified from material safety data sheets obtained from hydraulic fracturing service companies. Products presented in Table 4-1 are mixed on-site into large volumes of water just prior to injection during the hydraulic fracturing process. Injected concentrations of these products are usually much more diluted (with varying degrees of dilution) than those of concentrated products provided by the fracturing fluid manufacturers. EPA estimated the concentrations of constituents of concern at the point of injection and 100 feet from an idealized fracture radius. According to a study of fracturing fluid recovery in coalbed methane wells, conventional flowback techniques recover between 60 - 70% of injected fluids. Using the most conservative assumptions, the estimated concentration of the indicator constituent, benzene, at the fracture edge is below the MCL.

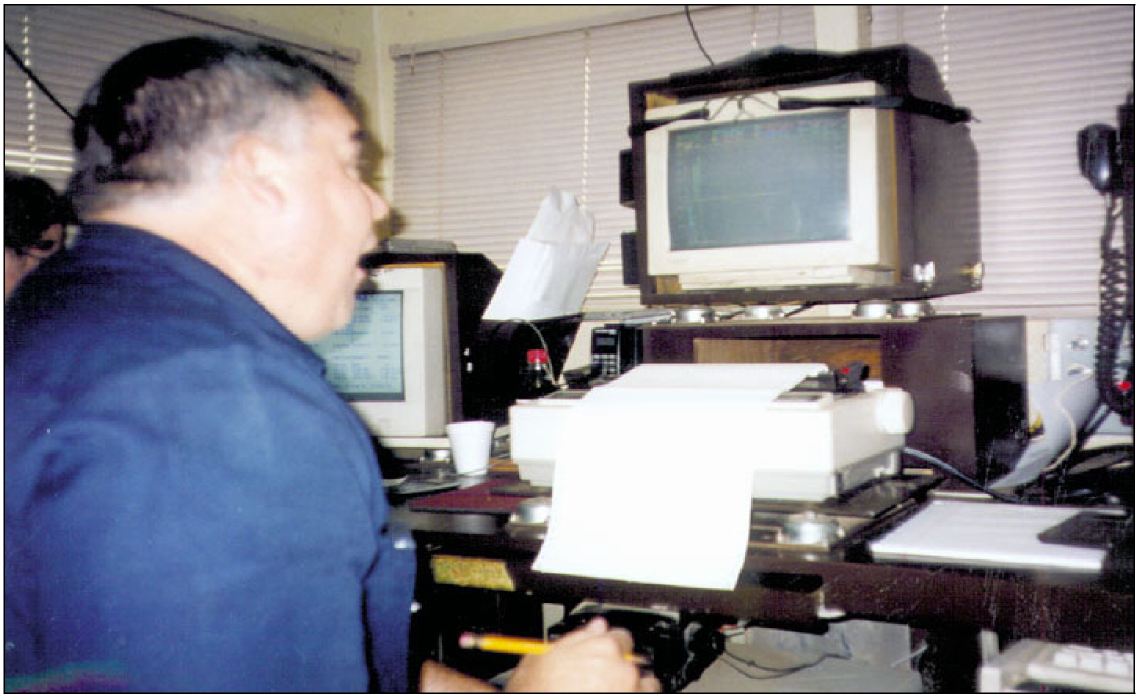
Figures 4-1 & 4-2. Liquid nitrogen tanker trucks transport gas to the site for N_2 foam fracturing. Nitrogen will travel through pipes to be mixed with water and a foaming agent at the wellhead prior to injection. The foam is used to create and propagate the fracture deep within the targeted coal seam.

Figures 4-3 & 4-4.
On-site chemical storage area is on a support truck. Fracturing fluid additives such as the foaming agent can be pumped directly from storage containers to mix tanks.

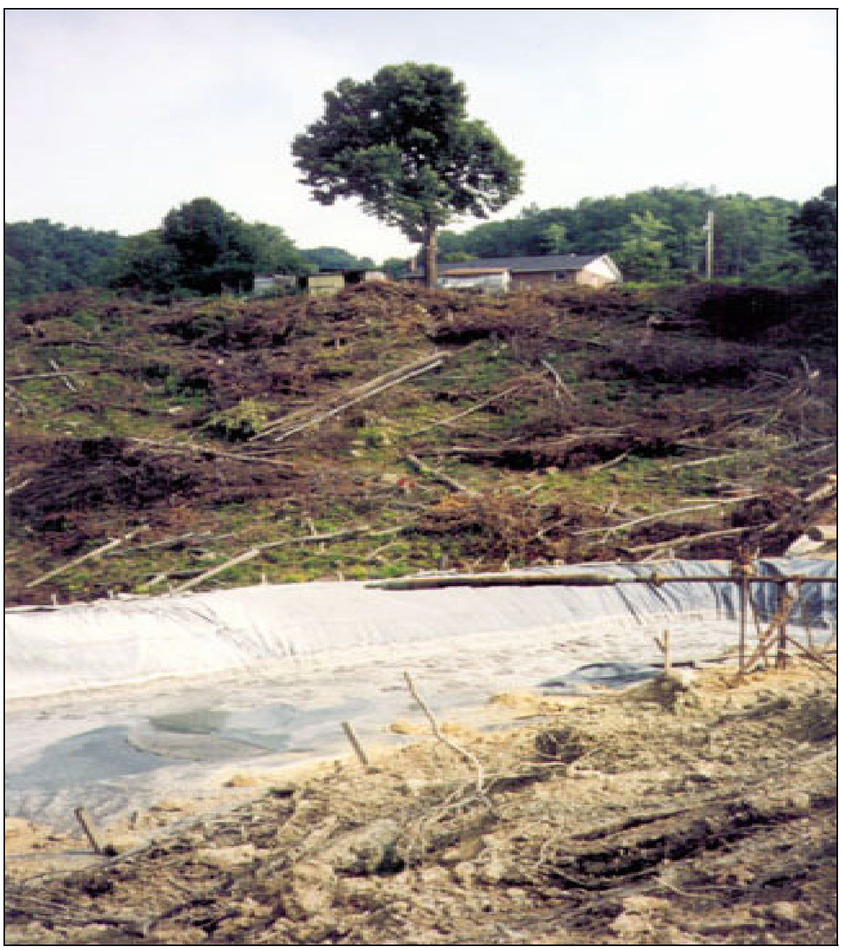
Figure 4-5.
The fracturing fluid (water with additives) is stored on site in large, upright storage tanks. Each tank contains mix water imported from offsite, or formation water extracted directly from the gas well.

Figure 4-6.
Gelled water is pre-mixed in a truck-mounted mixing tank. Photograph shows a batch of linear, guar-based gel. This gel is used to transport the sand proppant into the fracture propagated by the N_2 foam treatment.

Figure 4-7.
The fracturing fluids, additives, and proppant are pumped to the wellhead and mixed just prior to injection. The flow rate of each injected component is monitored carefully from an on-site control center.



Figures 4-8 & 4-9.
Electronic monitoring systems provide constant feedback to the service company's operators. Fluid flow rates and pressure buildup within the formation are monitored to ensure that fracture growth is safe and controlled.



Figures 4-10 & 4-11. Fluid that is extracted from the well is sprayed through a diffuser and stored in a lined trench until it is disposed of off-site or discharged.